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RPPR Final Report
as of 19-Apr-2018

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1. Rimoldi, M.; Howarth, A. J.; DeStefano, M. R.; Lin, L.; Goswami, S.; Li, P.; Hupp, J. T.; Farha, O. K. Catalytic Zirconium/Hafnium-Based Metal-Organic Frameworks ACS Catal. 2017, 7, 997-1014.
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11. Beyzavi, M. H.; Vermeulen, N. A.; Zhang, K. N.; So, M.; Kung, C. W.; Hupp, J. T.; Farha, O. K. Liquid-Phase Epitaxially Grown Metal-Organic Framework Thin Films for Efficient Tandem Catalysis through Site-Isolation of Catalytic Centers Chempluschem 2016, 81, 708-713.

Honors and Awards: •Farha was named by Clarivate Analytics One of the “Highly Cited Researchers”, (2017)

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- SCOPUS “Highly Cited Researcher” in Materials Science, (2016)
- Hupp was named by Clarivate Analytics One of the “Highly Cited Researchers”, (2017)

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PARTICIPANTS:

Participant Type: PD/PI

Participant: omar k farha 9680731

Person Months Worked: 1.00

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Project Contribution:

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Funding Support:

PIs: Farha & Hupp

Institute: Northwestern University, Chemistry Department

Abbreviations:

MOF = metal-organic framework

Ce = Cerium

Zr = Zirconium

UiO = University of Oslo

DMNP = dimethyl 4-nitrophenyl phosphate

GD = Soman = *O*-Pinacolyl methylphosphonofluoridate

Br=Bromine

CEES=2-chloroethyl ethyl sulfide

CEESO=2-chloroethyl ethyl sulfoxide

PEI = polyethyleneimine

MMM = mixed-matrix membrane

PIM = polymer of intrinsic microporosity

[a] Accomplishments and Summary:

(I) A Ce(IV)-based metal-organic framework (MOF) has been tested for the hydrolysis of a nerve agent simulant and the nerve agent, soman (GD) for the first time. Degradation half-lives of 8 min and 3 min were found for the simulant and nerve agent, respectively when using an N-ethylmorpholine buffer solution. A heterogeneous polyethyleneimine buffer was also used with the Ce-MOF catalyst and resulted in even faster hydrolysis of the simulant ($t_{1/2} = 4.5$ min). These results highlight the efficiency of Ce(IV)-based MOFs for hydrolysis of phosphate-ester based nerve agents.

We recently demonstrated that Zr₆-cluster-containing MOFs in the UiO

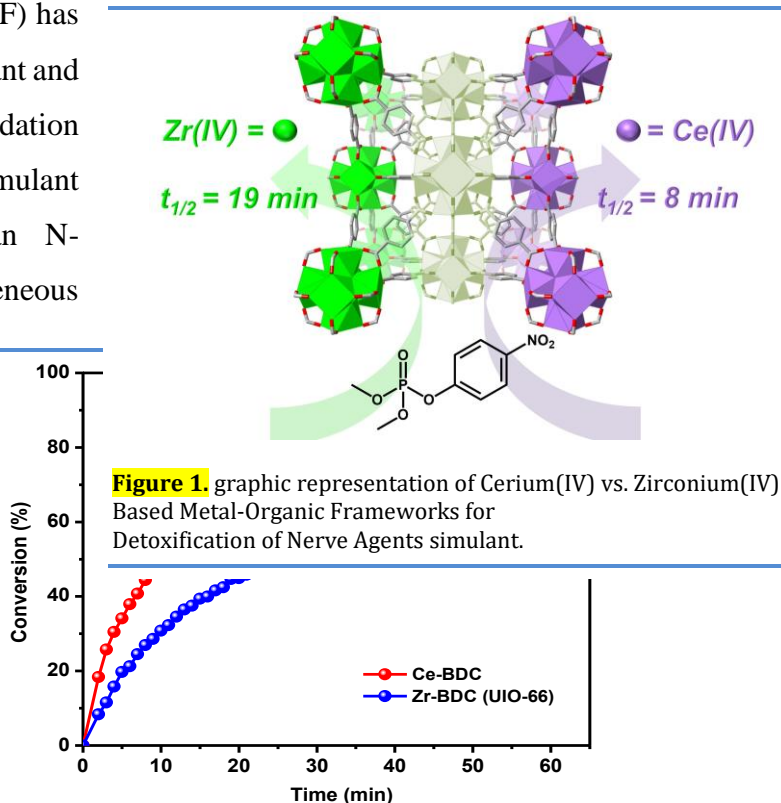


Figure 2. Hydrolysis profiles of DMNP with Ce-BDC (red circle) and UiO-66 (blue circle).

family has excellent hydrolysis rates towards organophosphate based nerve agents. In light of these findings, it is of interest to study MOFs containing different metal ions that can provide similar connectivity to that of the Zr_6 cluster but different ligand exchange rates and/or Lewis acidity while maintaining a similar oxidation state. Although there is no direct comparison of ligand exchange rates on Zr(IV) versus Ce(IV), it has previously been reported that Ce(IV) complexes show superior rates of phosphonate ester bond cleavage compared to Zr(IV) analogues in homogeneous form. The unprecedented activity of Ce(IV) has been attributed to the role of the Ce(IV) 4f orbitals which can mix with the orbitals of the P=O bond to form hybrid orbitals. This gives rise to a penta-coordinate intermediate which is susceptible to nucleophilic attack. Although this is very promising, Ce(IV) ions tend to form polymeric metal-hydroxo precipitates at pH > 4 which limits the potential of homogeneous Ce(IV) catalysts. Since Ce(IV) ions are stabilized in a $[Ce_6O_4(OH)_4]^{12+}$ node, Ce-UiO-66 should not suffer from metal-hydroxo precipitation. We postulated that Ce-UiO-66 would therefore show enhanced hydrolysis rates for DMNP compared to UiO-66 given that Ce(IV) shows superior activity to Zr(IV) under homogeneous conditions.

Potentiometric pH titrations show that Ce-UiO-66 and UiO-66 (HCl synthesis) have similar densities of defect sites. Additionally, DRIFTS spectra revealed that the sharp peak at 3674 cm^{-1} corresponding to the terminal -OH groups on the Zr_6 -node of UiO-66 is shifted to 3646 cm^{-1} in Ce-UiO-66 which highlights the difference in binding strength of the terminal -OH groups to Ce(IV) vs. Zr(IV).

Conversion profiles for both Ce-UiO-66 and UiO-66 are shown in [Figure 2](#). Initial rate calculations reveal that Ce-BDC substantially reduces the DMNP half-life, from 19 min to 8 min. It is worth noting that particle size plays a significant role in hydrolysis rates, especially for UiO-66 type MOFs. The Ce-UiO-66 used in this example consists of larger particles compared to UiO-66. Therefore, it is expected that the actual difference in hydrolysis rate might be even more drastic if the particle size could be easily decreased.

After observing the fast rate of DMNP hydrolysis using Ce-UiO-66, the next step was to test Ce-UiO-66 as a catalyst for the hydrolysis of the actual CWA, Soman (*O*-Pinacolyl methylphosphonofluoridate, also known as GD) ([Figure 3](#)). The half-life for the degradation of GD using Ce-UiO-66 was observed to be 3 min.

While Ce-BDC presents promising hydrolysis rates for DMNP as well as GD in an N-ethylmorpholine buffering solution, the use of liquid buffer must be eliminated for applications such as protective suits and masks. We recently demonstrated that polyethyleneimine (PEI), a linear polymer with repeating units composed of amine groups and carbon spacers, can be mixed with a MOF catalyst and employed as a heterogeneous buffer resulting in hydrolysis rates comparable to those found using N-ethylmorpholine solutions. With these results in hand, we prepared the PEI/ Ce-UiO-66 mixtures with different amounts of PEI to optimize the amine loading. We previously showed that the hydrolysis reaction with PEI alone in water is negligible. Under optimized conditions,

a shorter half-life was observed using PEI compared to N-ethylmorpholine (4.5 vs. 8 min) (Figure 4). This highlights the role of primary amines in the hydrolysis mechanism and points to a role for the buffer beyond just controlling the solution hydroxide concentration.

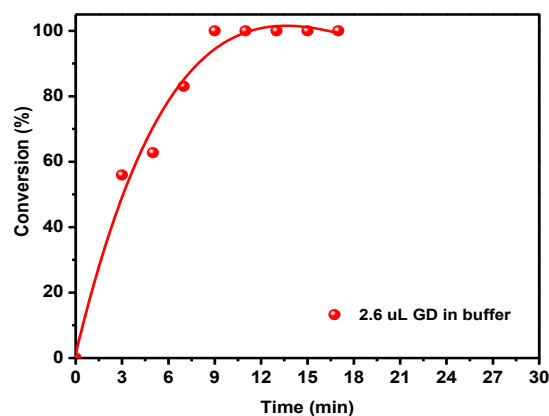


Figure 3. Hydrolysis profiles of GD with Ce-BDC in N-ethylmorpholine buffer solution.

(II) We have previously shown that Zr-

based MOFs are promising candidates for photosensitizer incorporation and subsequently for the catalytic and selective oxidation of sulfur

mustard using singlet oxygen.

Using different organic struts

comprising porphyrin¹¹¹¹¹ or

pyrene moieties, selective

(photos-sensitized) oxidation

of the sulfur mustard simulant

CEES to CEESO was

observed with half-lives of 13

or 6 min, respectively. While

the structural organic linkers

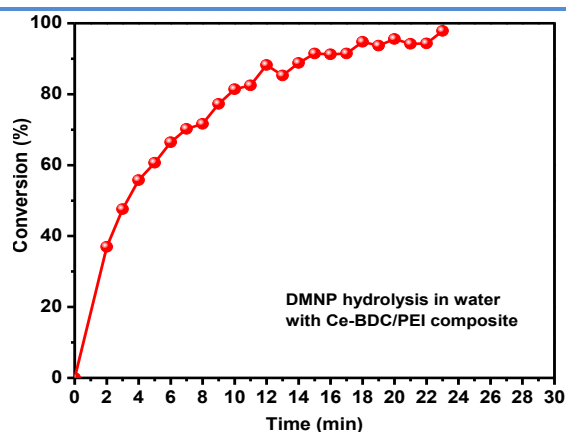


Figure 4. Hydrolysis profiles of DMNP with Ce-BDC/PEI composite in the presence of different amount of PEI.

of MOFs can be employed as photosensitizers, non-structural ligands can also be incorporated in Zr-MOFs, most notably by solvent assisted ligand incorporation (SALI). We have recently reported the incorporation of a fullerene-based photosensitizer for singlet oxygen into a Zr-based MOF via SALI and the resulting material showed a remarkable half-life for CEES oxidation of 3.5 min. However, fullerenes are synthetically challenging to produce and modify due to their low solubility and they have poor optical and electronic tunability²²² [ENREF 2](#)²²², which limits the ability to study fullerenes further for this application. It is therefore necessary to seek new materials for the detoxification of CEES (and hence sulfur mustard) that are even faster. Hereby, we demonstrate fast and selective detoxification of a mustard gas simulant (CEES) using NU-1000

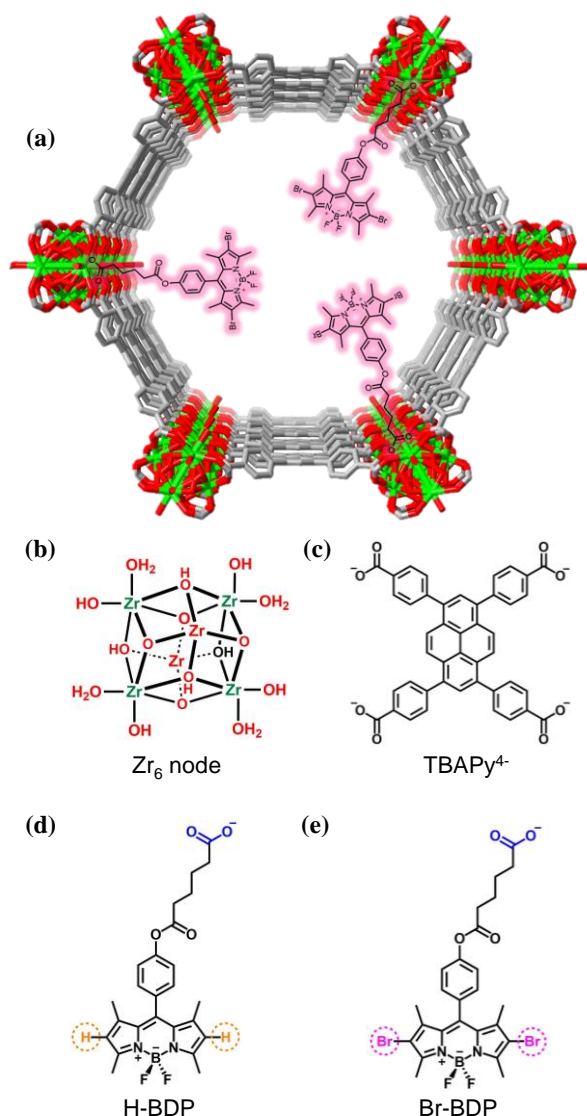


Figure 5 a) Schematic representation of Br-BDP@NU-1000; b) Zr_6 node of NU-1000, with SALI-displaceable aqua and hydroxy ligands shown in green; c) structure of organic linker of NU-1000, d) H-BDP e) Br-BDP.

modified with a highly tunable BODIPY chromophore (Figure 5). As depicted in Figure 5, we installed a carboxylic acid terminated chain on the meso position of the BODIPY chromophore which allows for the incorporation of BODIPY in NU-1000 by tethering the ligand to the Zr_6 -node. BODIPY was chosen as a chromophore for singlet oxygen generation due to its facile synthesis, ease of tunability and high solubility in numerous organic solvents, including solvents suitable which makes SALI. It is well-documented that functionalizing BODIPY with heavy atoms (*e.g.*, bromine or iodine) increases its efficiency as a photosensitizer for singlet oxygen due to enhanced intersystem crossing, *i.e.* photo-excited BODIPY singlet to excited triplet state conversion. Therefore, we synthesized carboxylic acid functionalized Br-BDP (Figure 5e) and compared it to Br-BDP after installation in NU-1000.

In Figure 6a, the efficacy of Br-BDP as compared is compared for the heterogeneous (MOF) versus homogeneous phase. Half-lives for CEES oxidation were observed to be approximately 2 min in each case (power density of irradiation = 450 mW.cm^{-2}).

As estimated by reaction half-lives, photo-oxidation based on Br-BDP@NU-1000 sensitization is nearly twice as fast as the fastest of the three previously investigated systems.

When compared to a porphyrin-based MOF catalyst run under 325 mW.cm^{-2} blue LED irradiation, the Br-BDP@NU-1000 sensitized oxidation (at equal light intensity) is about 5x faster half-life under equal irradiation power. Notably, even very low photocatalyst loadings (0.2 mol % Br-BDP@NU-1000) proved effective for CEES degradation by dioxygen.

The structural integrity of Br-BDP@NU-1000 before and after catalysis was confirmed using powder X-ray diffraction (PXRD), while scanning electron microscopy (SEM) revealed that the morphology of the crystals was unchanged (Figure 6b). An SEM-EDX line scan analysis performed on a crystal of Br-BDP@NU-1000 shows an unvarying ratio of Br to Zr, implying that Br-BDP is homogeneously distributed in the MOF. Furthermore, the recyclability of Br-BDP@NU-1000 was tested over four cycles, irradiating for 9 min each time (Figure 6c).

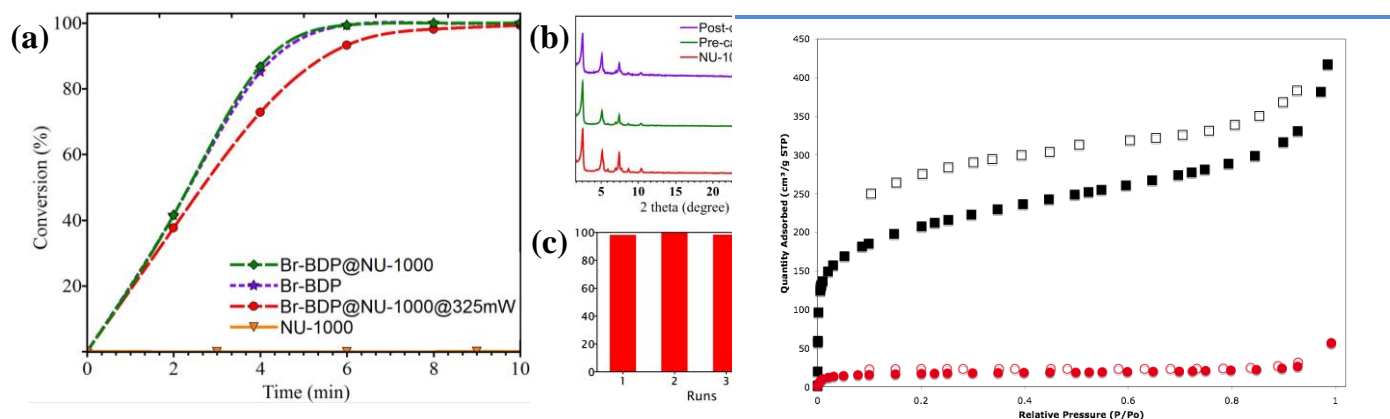
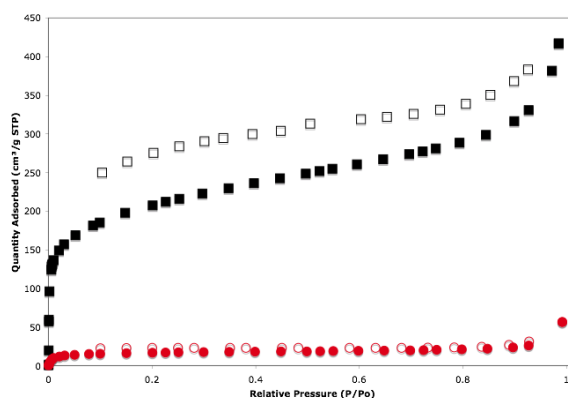


Figure 6. a) Comparison of oxidation of CEES with Br-BDP in homo/1 phase and NU-1000 under 450 mW.cm⁻² green light. Comparison efficiency of Br-BDP@NU-1000 under 325 mW and 450 mW light power. b) X-ray diffraction patterns of NU-1000, Br-BDP@NU-1000 and Br-B after catalysis. c) The reusability of the catalyst Br-BDP@NU-1000 (1 μmol) over four successive injections of CEES (0.2 mmol) into the same reaction vial.

Figure 8. N₂ adsorption profiles of PIM-1 (black squares) and PIM-1-EA (red circle).



In conclusion, we have observed facile incorporation (via SALI) of a very efficient and, in principle, chemically tunable photosensitizer, Br-BDP, into a stable Zr-based MOF. Photo excitation catalyzes the conversion of ground-state (triplet) oxygen to reactive singlet oxygen and, in turn, the fast and selective oxidation of the sulfur mustard simulant, CEES, to the less toxic sulfoxide product, CEESO. Notably, the Br-BDP-functionalized MOF retains crystallinity under catalysis conditions. Importantly, the photooxidation method makes use of readily available and inexpensive LEDs, synthetically tunable BODIPY molecules, and a simple incorporation method (SALI) which should enable screening of a wide range of BODIPY and related chromophores as photosensitizers for sulfur-mustard detoxification.

(III) For the above mentioned reasons, we are interested in using heterogeneous buffer systems and we have already successfully employed the amine containing linear polymer chains as pH mediators. However, using porous polymers could enhance the overall performance of the composite system since the intrinsic porosity provided by porous polymer would allow for substrate and/or product diffusion as opposed to non-porous linear polymer chains. Therefore it is of interest to study porous polymers containing different amine functionalities that can also be processed into films/membranes.

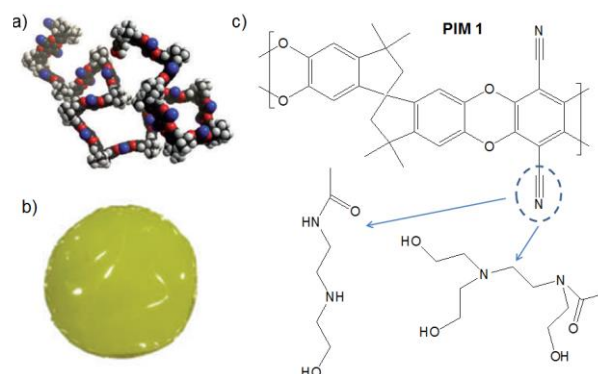


Figure 7. a) Molecular model for a fragment of a polymer of intrinsic microporosity, PIM-1, b) photograph of an amorphous PIM-1 film (right) cast from tetrahydrofuran solution and c) Amine-functionalized PIM-1.

PIM-1 comprised of fused ring sequences interrupted by spiro centers has a large surface area and can be processed into a film and can be functionalized with secondary or tertiary amines (Figure 7). Treatment of PIM-1 with ethanolamine produced the functionalized material PIM-1-EA. DRIFTS spectra revealed that the sharp peak at 2240 cm^{-1} corresponding to the terminal $-\text{CN}$ groups on PIM-1 had nearly disappeared suggesting full conversion. However, the porosity of the functionalized PIM is diminished as N_2 adsorption and BET surface area are reduced from 718 m^2g^{-1} to 64 m^2g^{-1} (Figure 8). The hydrolysis of DMNP with NU-1000 and PIM-1-EA conducted under conditions similar to those previously reported for NU-1000 in *N*-ethylmorpholine buffer solution except using PIM-1-EA as a heterogeneous buffer and was monitored by *in-situ* ^{31}P NMR spectroscopy with only water as solution media. Unfortunately, no detectable signals associated with the hydrolysis byproducts were observed even after 1 hour. Two other PIMs functionalized with amidoxime and Tröger's base (PIM-1-AO and PIM-TB-9) possessing adequate porosities (480 m^2g^{-1} and 677 m^2g^{-1} respectively) were utilized as buffers in the hydrolysis of DMNP with NU-1000. These porous polymers proved like the previous heterogeneous buffer system to not induce hydrolysis of DMNP. While the significant loss in porosity may contribute to the inhibition of hydrolysis, the inherent hydrophobicity of porous organic polymers limits their use as heterogeneous buffer systems. Indeed, the hydrophilic NU-1000 and heterogeneous buffers were observed to phase separate under the aqueous conditions.



Figure 10. NU-1000-PEI MMM (NU-1) being used as a syringe filter for the hydrolysis of DMNP.

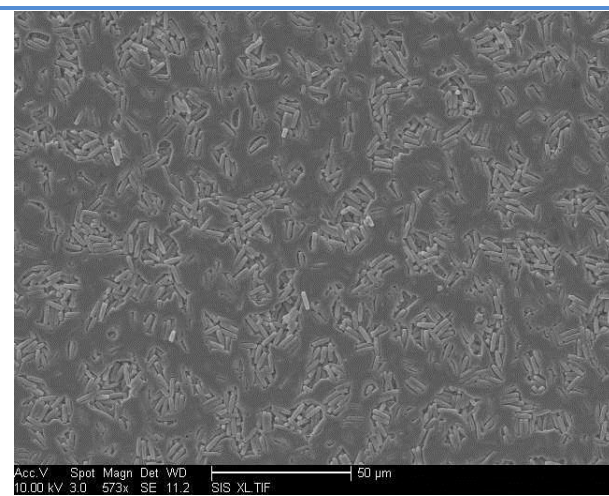


Figure 9. SEM of MMM NU-1.

Given the separation observed in the previous study we sought to utilize mixed-matrix-membranes (MMMs) composed of PDVF/PEI/NU-1000 mixtures. Our collaborators at UCSD prepared MMMs with different amounts of NU-1000 and PEI through a drawdown coating process. We postulated that the MMMs would generate a homogeneously disperse NU-1000/PEI composite and facilitate hydrolysis of DMNP. However, as observed by SEM images the composites generate pockets of NU-1000 with surrounding PDVF/PEI polymers (Figure 9). We utilized the NU-1000-MMMs (NU-1, containing 20% NU-1000, 46% PEI, 33% PVDF) in the hydrolysis of DMNP under conditions similar to those previously reported for NU-1000 in *N*-ethylmorpholine buffer solution and with

only water as solution media, however, no detectable hydrolysis products were observed by *in-situ* ^{31}P NMR spectroscopy.

In a previous study, dehydrated NU-1000 (NU-1000-dehydrated) showed remarkably enhanced catalytic activity for the hydrolysis of DMNP yielding a half-life of $< 2\text{min}$ in 0.45 M N-ethylmorpholine buffer solution. In this regard, we sought to see if NU-1000-dehydrated/PEI/PVDF MMMs could hydrolyze DMNP in both N-ethylmorpholine buffer solution and water. The hydrolysis of DMNP with (NU-d1, containing 22% dehydrated-NU-1000, 49% PEI, 30% PVDF) under conditions similar to those previously reported for NU-1000 again failed to generate any hydrolysis products by *in-situ* ^{31}P NMR spectroscopy. Hydrolysis of the simulant was attempted under syringe-pump conditions where NU-1 or NU-1d membranes (Figure 10) were slowly passed with solutions of buffer (N-ethylmorpholine) or water containing DMNP. Aliquots were collected and monitored periodically up to 20 minutes however no signs of hydrolysis were observed by ^{31}P NMR spectroscopy.

[b] Awards in Year 4:

- Farha was named by Clarivate Analytics One of the “Highly Cited Researchers”, (2017)
- Farha named the “Kavli Emerging Leader Lecturer” for the ACS National Meeting in Philadelphia (2016)
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[c] Publications in year 4:

1. Rimoldi, M.; Howarth, A. J.; DeStefano, M. R.; Lin, L.; Goswami, S.; Li, P.; Hupp, J. T.; Farha, O. K. Catalytic Zirconium/Hafnium-Based Metal-Organic Frameworks *ACS Catal.* **2017**, 7, 997-1014.
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